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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Siloxane Elastomers

We, MIDLAND SILICONES LIMITED, a British Company, of 68 Knightsbridge, London, S.W.1., do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improved vulcanisable organopolysiloxane elastomeric compositions and to a process for their preparation.

When organopolysiloxanes which are convertible to the solid elastic state are compounded with certain silica fillers such as fume silicas and precipitated silicas the compounded mass becomes tough and difficult to process. This toughness is due to the formation of 'structure' and is the result of undesirable interaction between reactive sites on the polymer and the filler. Various methods have been proposed for overcoming this problem. For instance, it has been proposed to treat the surface of the silica with hydroxylated organosilicon compounds such as siloxanols and silanols. Other methods which have been suggested include treating the silica filler with sulphur dioxide prior to its incorporation with organosilicon polymer.

Although elastomers containing reinforcing silicas as fillers may now be prepared fairly conveniently and have found wide commercial acceptance, there is a continuing effort to improve the physical properties of such elastomers. One known method which is said to improve the physical properties of vulcanised silica filled organopolysiloxanes comprises heating a mixture of an organopolysiloxane, a silica filler and an organic amine or amine salt prior to vulcanisation. However, such a process leads to an elastomeric composition which is characterised by a high degree of structure formation resulting in a composition which can be further processed only with difficulty.

We have now unexpectedly found that the formation of structure in reinforcing silica filled organopolysiloxane stocks may be mini-

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mised by incorporating therein an organosilicon compound which is a disilazane or a silylamine, the inclusion of the defined organosilicon compound also leading to an elastomer having in many cases, significantly improved physical properties, and particularly exhibiting improved tear resistance.

According to the present invention there is provided a vulcanisable composition which comprises a mixture of (1) an organopolysiloxane convertible to the solid elastic state, (2) a finely divided reinforcing silica filler and (3) a disilazane and/or a silylamine.

The present invention also provides a vulcanisable composition which comprises a mixture of (1) an organopolysiloxane convertible to the solid elastic state and (2) a finely divided reinforcing silica filler which has been treated with a disilazane and/or silylamine.

The invention also includes within its scope a process for the preparation of vulcanisable compositions which comprises mixing (1) an organopolysiloxane convertible to the solid elastic state (2) a finely divided reinforcing silica filler and (3) a disilazane and/or a silylamine.

The convertible organopolysiloxanes are preferably linear or substantially linear siloxane polymers containing an average of from 1.95 to 2.05 and preferably from 1.99 to 2.01 organic groups per silicon atom. Such organopolysiloxanes may vary from viscous liquids to stiff non flowing gums and can be represented by the unit general formula R_nSiO_{4-n} wherein each R is a monovalent

hydrocarbon radical or a monovalent substituted hydrocarbon radical and n has a value between 1.95 and 2.05. The preferred polymers are essentially linear in character, that is they comprise substantially 100 per cent diorganosiloxane units with or without the presence of end-blocking units of the formula $R_3SiO_{1/2}$. However, the siloxane polymer may

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if desired contain up to a few per cent of $\text{RSiO}_{3/2}$ or $\text{SiO}_{4/2}$ units provided it remains convertible to the solid elastic state. The nature of the organic substituents, that is the R groups, present in the organopolysiloxane is not critical and they may comprise for example any one or more of alkyl radicals such as methyl, ethyl and propyl, alkenyl radicals such as vinyl and allyl, aryl radicals such as phenyl and naphthyl and substituted hydrocarbon radicals such as chlorophenyl, trifluoropropyl or cyanopropyl radicals. As a matter of manufacturing convenience it is preferred to employ organopolysiloxanes in which the organic substituents are selected from one or more of methyl, vinyl and phenyl radicals. Particularly preferred are copolymeric diorganopolysiloxanes containing mainly methyl radicals as substituents and in which any remaining substituents comprise phenyl and/or vinyl radicals. It will of course be understood that when certain specific properties, for instance solvent resistance are required in the finished elastomer it may be desirable to employ a polymer which contains for example, fluoroalkyl or cyanoalkyl radicals.

The methods of preparation of suitable convertible organopolysiloxanes and their use in the manufacture of organopolysiloxane-based elastomers are now well known.

The silica fillers employed in the compositions of this invention are those reinforcing silicas of fine particle size such as may be obtained by the fume or precipitation processes. Such silicas are produced having a very high surface area to weight ratio and containing reactive groups, which are probably hydroxyl groups, attached to the silicon atoms at its surface. The silica fillers may be employed in proportion of from 15 to 150 parts by weight, preferably from 20 to 85 parts, per 100 parts by weight of the convertible organopolysiloxane.

The surface treating agents for the silica, that is, ingredient (3) of the vulcanisable compositions, are disilazanes and/or silylamines. The disilazanes are organosilicon compounds

containing the linkage $\equiv \text{Si} - \text{N} - \text{Si} \equiv$ the remaining valencies of the nitrogen atoms being satisfied by organic radicals and/or hydrogen atoms and the remaining valencies of the silicon atoms being satisfied by organic radicals. Specific examples of suitable disilazanes are hexamethyldisilazane, divinyltetramethyl disilazane and diphenyltetramethyl disilazane.

Also suitable as surface treating agents for the silicas in the compositions of this invention are the silylamines. These compounds have the general formula



where each R' is a hydrogen atom, a hydrocarbon radical or a substituted hydrocarbon

radical and each R'' is a hydrogen atom or a hydrocarbon radical. Silylamines in which the R' and R'' groups are lower alkyl groups, such as methyl and ethyl are unstable at normal temperatures and tend to condense to form disilazanes. However, as already indicated, the disilazanes which are formed are also operative as treating agents for the silica. Examples of silylamines which may be employed therefore are triphenylsilylamine, diphenylmethylsilylamine, (triethylsilyl) dimethylamine and trimethyl-N-ethyl silylamine.

The quantity of disilazane or silylamine employed will depend mainly upon the nature and quantity of the reinforcing silica filler. Normally from 5 to 50 parts by weight for every 100 parts by weight of the convertible organopolysiloxane is sufficient to achieve the desired effect.

If desired the silica may be treated with the disilazane or the silylamine prior to incorporating the silica with the convertible organopolysiloxane. This method merely involves adding the disilazane or silylamine to the silica and may be most conveniently employed when the silicon-nitrogen compound is a liquid at the mixing temperature but can also be employed when a mutual organic solvent is present. However this separate treating step is not essential as the disilazane or silylamine may be added during the compounding of the organopolysiloxane and, the silica filler, for example by simply mixing in the cold the convertible organopolysiloxane, the silica filler and the silicon-nitrogen compound. Following the mixing step the material may advantageously be heated to remove volatile bases which are evolved during the mixing step, and also to remove any excess of the silicon-nitrogen compound. The reactivities of the silicon-nitrogen compounds vary and in the case of the less reactive materials such a heating step may be necessary during mixing or following it to promote or complete the reaction, the temperature achieved during the operation preferably not exceeding 300°C . When the silicon-nitrogen compound employed is volatile at the mixing temperature it may be necessary to provide the mixing apparatus with a reflux device to avoid excessive loss of the volatile material during the mixing or heating stage.

In view of the efficiency of the disilazanes as treating agents the compositions of this invention exhibit little or no hardening during the mixing operation or during storage prior to vulcanisation. Further, the vulcanised elastomers possess good physical properties particularly tear resistance.

When appropriate, other fillers and additives may be incorporated into the compositions of this invention. For example fillers such as titanium dioxide, magnesium oxide and non-reinforcing silicas such as diatomaceous earth may be employed in addition to the structure-inducing silicas. Other additional

ingredients may include heat stability additives and pigments.

Vulcanisation of the compositions of this invention may be carried out by any of the techniques common to the art for example by means of organic peroxides such as benzoyl peroxide, 2,4. dichlorobenzoyl peroxide and dicumyl peroxide, by means of high energy radiation or by any of the cold vulcanising techniques for example by incorporating in the composition an alkyl silicate or polysilicate and a siloxane condensation catalyst.

The invention is illustrated by the following examples in which the physical properties of the vulcanised elastomers were measured according to the methods laid down B.S. 903, Part A7, 1957, Part A2 1956 and Part A3, 1956.

EXAMPLE 1

100 parts of a copolymeric siloxane gum comprising 7.5% by weight of diphenylsiloxane, 92.35% by weight of dimethylsiloxane and 0.15% by weight of methylvinylsiloxane was compounded with 40 parts of a fume silica having a surface area of 300 square metres per gram (measured by the B.E.T. nitrogen adsorption method) and 20 parts of hexamethyl disilazane employing conventional rubber mixing equipment. The system was

then sealed and the mix heated under reflux for 4 hours. At the end of this heating period the temperature was raised to 180°C for one hour to remove volatile material. The mix was identified as Stock A.

When the stock had cooled a portion of it was compounded with 2 parts (per 100 parts of gum) of a 40% paste of 2:4 dichlorobenzoyl peroxide in a silicone fluid, the remainder of the mix being stored. The portion of the stock containing the vulcanising agent was vulcanised by pressing between steel sheets for 5 minutes at 115°C and further cured for 24 hours at 250°C.

In a similar manner a further composition was prepared employing as ingredients 30 parts of trimethyl N-ethyl silylamine in place of the hexamethyl disilazane, 100 parts of a copolymer containing 99.835% by weight of dimethylsiloxane and 0.165% by weight of methylvinylsiloxane and 40 parts of a fume silica (300m²/g B.E.T. surface area). This was identified as Stock B and vulcanised and post cured in the manner described for Stock A.

Physical properties of both Stock A and Stock B were measured and the following results obtained.

		Hardness BS°	Tensile Strength in lb/sq. in.	Per cent elongation at break	Tear Strength (lbs)
Stock A	Press Cured 5 min/115°C.	38	1450	580	19.4
	Post Cured 24 hr/250°C.	45	1240	400	12.3
Stock B	Press Cured 5 min/115°C.	35	1480	685	18.8
	Post Cured 24 hr/250°C.	38	1055	530	12.5

When the stored compounded stocks were examined after 3 months both Stock A and Stock B were found to exhibit little or no structure formation. The stocks were easily processable and each banded to a cohesive sheet in less than a minute when milled on a two roll mill.

EXAMPLE 2

50 parts of a fume silica having a surface area of 300 m²/gram (B.E.T.), 50 parts of toluene and 25 parts of hexamethyl disilazane were charged to a mixer and the system then heated under reflux for 4 hours. At the end of this heating period the mass was allowed to cool and was then intimately compounded with 100 parts of a copolymeric siloxane gum

comprising 86.845% by weight of dimethylsiloxane, 13% by weight of phenylmethylsiloxane and 0.155% by weight of vinylmethylsiloxane. During the compounding operation the temperature of the mix was raised to 180°C and a vacuum applied in order to remove volatile material.

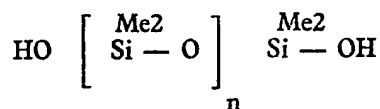
When cool, one portion of the stock was stored, the remainder being compounded with 2 parts (per 100 parts of polysiloxane gum) of a 40% paste of a 2:4 dichlorobenzoyl peroxide. This portion of the stock was vulcanised and cured according to the method described in Example 1 and the following physical properties obtained for the stock.

	Hardness BS°	Tensile Strength in lb/sq. in.	Per Cent elongation at break	Tear Strength (lbs.)
Press Cured 5 min/115°C	48	1435	510	21.9
Post Cured 24 hr/250°C.	70	963	225	9.7

After 3 months the stored material was found to exhibit no structure formation and banded to a cohesive sheet after a milling time of less than one minute.

For purposes of comparison a stock was compounded by mixing together 100 parts of

the copolymeric phenylmethylvinyl siloxane gum employed above, 50 parts of a fume silica having a B.E.T. surface area of 300 m²/g. and 17.5 parts of a low molecular weight hydroxylated siloxane of the general formula



Where n has an average value of between 10 and 17 and Me is a methyl radical. The stock was further compounded with 0.8 parts of 2,4 dichlorobenzoyl peroxide as curing agent and employed to prepare vulcanised sheets by moulding between platens for 5 minutes at

115°C. The physical properties of the vulcanised rubber were measured following the press cure and oven post cures of 4 hours and 24 hours at 250°C. The results obtained were as follows:

	Hardness BS°	Tensile Strength (p.s.i.)	Elongation at break (%)	Tear Strength (lb.)
Press Cure 5 min/115°C.	53	1100	320	11.5
Post Cure 24 hr/250°C.	66	820	300	9.2

EXAMPLE 3

100 parts of the phenylmethylvinyl polysiloxane gum employed in Example 2, 40 parts of a high surface area fume silica and 20 parts of hexamethyl disilazane were compounded on a two-roll mill at room temperature for two hours. The temperature of the rolls of the mill was then raised to 150°C

and the milling continued for a further 1½ hours to remove excess hexamethyl disilazane.

When cool, part of the stock was stored and the remainder was compounded with 2:4 dichlorobenzoyl peroxide, vulcanised and cured as described in Examples 1 and 2. The physical properties obtained for the vulcanised and cured rubber are shown below.

	Hardness BS°	Tensile Strength in lb/sq. in.	Per Cent elongation at break	Tear Strength (lbs.)
Press Cured 5 min/115°C.	42	1470	600	20.0
Post Cured 24 hr/250°C.	50	1235	300	12.1

After a period of 3 months the stored mix was found to band easily on a two-roll mill requiring a milling time of less than one minute to form a cohesive sheet.

EXAMPLE 4

100 parts of the methylvinyl polysiloxane gum employed in Stock B in Example 1, 40 parts of a fume silica having a B.E.T. sur-

face area of 300 m²/g and 20 parts of symmetrical tetramethyl divinyl disilazane was charged to a mixer and the system heated under reflux for 4 hours. The temperature was then raised to 180°C and a vacuum applied in order to remove volatile material.

Part of the stock was stored and part was compounded with 2:4 dichlorobenzoyl peroxide, vulcanised and tested according to the procedure described in Example 1. The following physical properties were obtained for the vulcanised rubber.

	Hardness BS°	Tensile Strength (lb./sq. in.)	Per Cent elongation at break	Tear Strength (lbs.)
Press Cured 5 min/115°C.	46	1020	510	15.8
Post Cured 24 hr/250°C.	52	950	270	7.3

The stored stock exhibited little or no structure formation when tested after 3 months storage.

EXAMPLE 5

100 parts of a phenylmethylvinyl polysiloxane as employed in Example 2 was compounded with 40 parts of a fume silica and 20 parts of symmetrical tetramethyl vinyl disilazane according to the procedure of Example 3.

When vulcanised and cured the rubber exhibited physical properties similar to those obtained in Example 4. The compounded and vulcanised stock had not hardened due to the formation of structure when examined after 3 months storage.

EXAMPLE 6

The anti-structure additive employed in this example was triethylsilylamine (C₂H₅)₃SiNH₂ and 20 parts of this additive was compounded with 100 parts of the phenylmethylvinyl polysiloxane gum of Example 2 and 40 parts of a fume silica (300 m²/g B.E.T. surface area) on a two-roll mill at room temperature for two hours. The excess amine was then removed by a further milling for two hours with the mill rolls maintained at a temperature of 150°C.

When compounded with 2:4 dichlorobenzoyl peroxide, vulcanised and cured the following physical properties were obtained.

	Hardness BS°	Tensile Strength (lb/sq. in.)	Per Cent elongation at break	Tear Strength (lbs.)
Press Cured 5 min/115°C	32	1340	610	16.8
Post Cured 24 hr/250°C.	46	770	250	5.7

The stock exhibited no tendency to harden on storage for a period of 3 months.

WHAT WE CLAIM IS:—

1. A process for preparing a surface-modified silica for use as a filler in organopolysiloxane elastomeric compositions, which comprises contacting a finely-divided reinforcing silica filler with disilazane and/or silylamine.

2. A surface-modified silica when prepared by the process claimed in claim 1.

3. A process for preparing a vulcanisable composition which comprises mixing (1) an organopolysiloxane convertible to the solid elastic state and (2) a surface-modified silica filler as claimed in claim 2.

4. A modification of the process claimed in claim 3 for the preparation of a vulcanisable

composition, comprising mixing together (1) an organopolysiloxane convertible to the solid elastic state, (2) a finely divided reinforcing silica filler and (3) a disilazane and/or a silylamine.

5. A process as claimed in claim 3 or claim 4 wherein there are present in the resulting mixture (1) 100 parts by weight of the convertible organopolysiloxane (2) from 20 to 85 parts by weight of the finely-divided reinforcing silica filler and (3) from 5 to 50 parts by weight of the disilazane and/or silylamine.

6. A process as claimed in any one of claims 3, 4, and 5 wherein the convertible organopolysiloxane is a copolymeric diorganopolysiloxane in which the organic substituents

comprise mainly methyl radicals any other substituents present being phenyl radicals and/or vinyl radicals.

- 5 7. A process as claimed in any one of claims 3 to 6 inclusive wherein the mixture is heated during or after the mixing operation to a temperature not exceeding 300°C.

- 10 8. A process for the preparation of a vulcanisable composition according to claim 3 or claim 4 substantially as described in any of the examples herein.

9. A vulcanisable composition prepared by the process claimed in any one of claims 3 to 8 inclusive.

10. A vulcanisable composition as claimed in claim 9 which also contains a vulcanising agent. 15

11. A composition as claimed in claim 10 wherein the vulcanising agent is an organic peroxide. 20

12. An elastomer which is the product of vulcanising the composition claimed in any one of claims 9 to 11 inclusive.

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